

XI. Polymer Research

PROPULSION DIVISION

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A. Permeability of Polymer Films and the Solubility Parameter, R. F. Landel

In the search for bladder materials, rather scant attention has been paid to some pertinent facets of elastomer behavior. The bladders should be reasonably flexible and have a low permeability. In general, these are incompatible requirements. Permeability P is defined as the rate of mass flow/cm²/cm thickness/unit time. It is actually the product of the diffusion coefficient D and the solubility S of the vapor in the material

$$P = DS \quad (1)$$

The quantities S and D can be examined separately.

The diffusion coefficient is determined by the internal mobility of the chains. Small molecules thread their way between the chains just as one solvent diffuses through another. The only way to reduce the diffusant mobility by modifying the polymer structure is to reduce the chain mobility, e.g., by raising the glass temperature or increasing the crosslinking in the elastomer. But both of these make the material harder and more leatherlike. Thus, any polymer whose flexibility originates in coop-

erative modes of motion of essentially liquid-like character will of necessity be permeable. Any search for new materials whose flexibility stems from this type of molecular motion should be rejected until some new principle of molecular dynamics is discovered to provide a theoretical basis for the search.

Fillers can reduce the diffusion rate by increasing the path length. Effectively, the sample has a smaller cross-sectional area for the vapor to diffuse through. Thus, leaf-like fillers such as mica and flake glass can be expected to be more beneficial on a volume per volume basis than more compact shapes. Van Amerongen (Ref. 1) found the diffusion of N₂ in natural rubber to be scarcely affected by various carbon blacks but was reduced by a factor of 4.9 by the inclusion of 20% by weight of mica. The reduction factors for H₂, O₂, and CO₂ were 4.5, 5.0, and 7.7, respectively.

Crystallites will also act as fillers in this context; therefore a partially crystallized polymer would be better than an amorphous system and a highly crystalline one better than a partially crystalline one. Thus, low density polyethylene, 65% crystalline, is eight times as permeable to N₂ or H₂O as high-density polyethylene, 85% crystalline (Ref. 2).

Even when some permeability is acceptable, however, there are rational guidelines to material selection based on S . The solubility of a substance in a polymer is determined by the intermolecular forces. In the absence of actual chemical attack by the solvent, these can be characterized by the solubility parameter δ . This quantity

is a measure of the energy required to separate a pair of molecules or chain segments in the liquid state. When $\delta_{\text{solvent}} = \delta_{\text{polymer}}$, the polymer will dissolve if it is not crosslinked; if it is crosslinked, it will swell and attain its maximum swelling. Thus, to prevent swelling, which enhances the diffusion constant, one should strive for the greatest possible mismatch in δ .

Table 1. Calculation of δ

Equations (Refs. 3, 4, and 5).		
(1) $\delta = \left[\frac{25\gamma}{(V_m^L)^{1/2}} \right]^{1/2}$		
where		
V_m^L = molar volume of liquid at 25°C		
γ = surface tension at 25°C, dynes/cm ²		
(2) $\delta = \left(\frac{\Delta H_v^* - (C_p^* - C_p^L)(T_b - T) - RT}{V_m^L} \right)^{1/2}$		
(3) $\delta = \left(\frac{\Delta H_v^* - RT}{V_m^L} \right)^{1/2}$ i.e., Eq. (2) without the heat capacity term.		
where		
ΔH_v^* = molar heat of vaporization at the boiling point		
ΔC_p = difference in molar heat capacities of vapor and liquid at the temperature T .		
V_m^L = molar volume of the liquid at temperature T , and T_b = boiling point, °K.		
Values of appropriate parameters		
Parameter	N ₂ H ₄	N ₂ O ₄
Heat of vaporization	9600 cal/g mole at 112°C	9110 cal/g mole at 21°C
Boiling point	114°C	18°C
C_p , liquid	25.67 cal/g mole/°C at 114°C	33.74 cal/g mole/°C at 18°C
C_p , vapor	13.96 cal/g mole/°C at 118°C	10.3 cal/g mole/°C at 77°F (25°C) (NO ₂ , 1.8 cal/g mole/°C at 18°C)
Surface tension	66.67 dynes/cm at 25°C	27.5 dynes/cm at 20°C
Density		
Anhydrous	1.007 g/cm ³	1.491 g/cm ³
Commercial	1.01	
Molecular weight	32.05 g/mole	92.02 g/mole
Molar volume	32.1 cm ³ /mole	61.8 cm ³ /mole

The value of δ for a polymer may not be known explicitly to a supplier of a given kind of polymer. However, he will usually have some indication of the swelling behavior in several common solvents, and the value of δ for these is generally known or easily estimated. Burrell and Immergut list the values for more than 240 solvents (Ref. 3). If the polymer swells in a solvent whose δ is close to that of the liquid to be retained in the bladder, it will probably be a poor choice and can be discarded without further testing.

Because the solubility aspects seem to have been neglected, we have calculated approximate values of δ for N₂H₄ and N₂O₄ from the equation and data given in Table 1. The results, given in Table 2, are not in particularly good agreement and are unusually high, compared to common solvents. On the other hand, the value for ammonia is 16.3, quite comparable to that calculated for hydrazine. Moreover, a plot of the values for low molecular weight mono amines as a function of the number of carbon atoms, when extrapolated to zero carbon content, also indicates that a very high value for N₂H₄ is to be expected (Fig. 1). Unfortunately, the δ values for the corresponding diamine series is not available, otherwise a similar plot could be made to obtain a more realistic confirmation of the calculated value.

To illustrate that such a plot is valid, and that end groups should contribute in a regular fashion, the δ values for *n*-paraffins and *n*-alcohols are also shown in Fig. 1. In the former case, the extrapolation shows that the expected value for hydrogen should be less than 4. The actual value is 3. From the curve for the alcohols, the

Table 2. Approximate solubility parameters for N₂H₄ and N₂O₄ at 25°C in (cal/cm³)^{1/2}

Reference (from Table 1)	N ₂ H ₄	N ₂ O ₄
Eq. (1)	15	11
Eq. (2)	18.1	11.3 (at 19°C, the b.p.)
Eq. (3)	16.8	

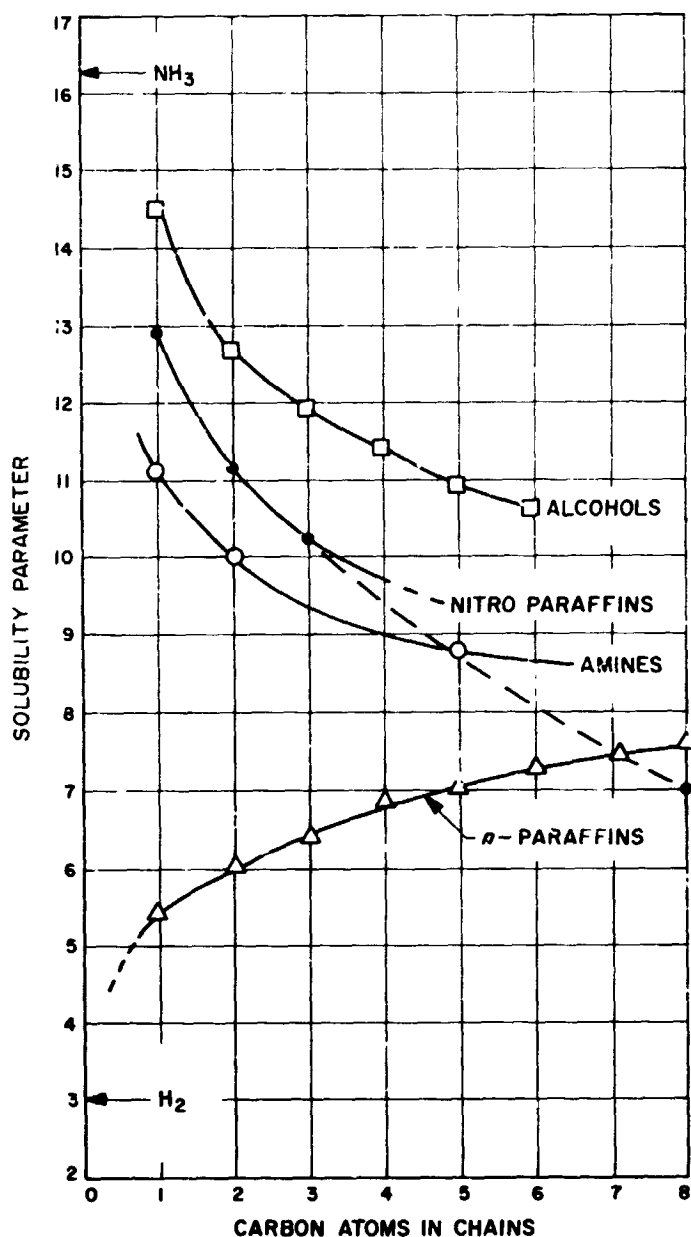


Fig. 1. Solubility parameters as a function of carbon content of *n*-paraffins and their primary hydroxy, amino, and nitro derivatives

expected value for water would be > 17 , and the actual value is 23.4.

Fig. 1 also contains data for the paraffinic nitro derivatives. (The value for 1-nitrooctane appears to be too low, since it lies below that of pure *n*-octane.) Extrapolation of the curve to zero carbon content indicates that the expected magnitude of δ for N_2O_4 is greater than 13, instead of the calculated value of 11 to 11.8. On the other hand, it should be realized that the structure of the NO_2 radical in N_2O_4 is different from that in nitro-compounds—the

main value of this plot, in the case of N_2O_4 , is a confirmation of the high calculated value. Hence, the values of 17.0 for N_2H_4 and 11.5 for N_2O_4 appear to be reasonable after all.

Table 3 gives a comparison of δ for several materials and the behavior of these with N_2H_4 , N_2O_4 , and 50/50 UDMH/ N_2H_4 .¹ The values of δ for UDMH have not yet been calculated. Thus, considering the N_2H_4 and UDMH/ N_2H_4 , it can be seen that the rubbers with low δ values tend to be more resistant. This suggests that nitroso rubber (a copolymer of tetrafluoroethylene, the monomer of Teflon, and trifluoronitrosomethane) with a δ value of 5.2 should be especially resistant to both N_2H_4 and N_2O_4 . In fact, it is not; nitroso rubber reacts with hydrazine.

Even amines, which are much weaker bases than hydrazine, will attack this polymer (and Viton, too) and can be used as crosslinking agents. This illustrates a weakness of the use of the solubility parameter as a screening tool—a large mismatch in δ is a necessary but not sufficient condition for the utility of an elastomer.

In this sense these elastomers are similar to the unsaturated hydrocarbon rubbers in the presence of N_2O_4 —according to their δ values they should be resistant to swelling, but in actual fact they are degraded. Such chemical reaction is quite a different phenomenon from simple dissolution and one in which δ values play no direct role. Similarly, both the Viton and nitroso gumstocks are stable in the presence of N_2O_4 , but the currently used amine curing systems introduce hydrocarbon-containing crosslinks and these, not the rubber, are oxidatively unstable. The recent chromium crosslinking method was created to avoid this problem.

There are some swelling anomalies in Table 3. Neither the butyl nor the nitroso rubbers, for example, ought to swell in N_2O_4 , according to the δ values, but they do. While some of the swelling may be the result of attack at the crosslinks, the polyisobutylene has no crosslinks at all and so should not have liquefied (presumably it was not chemically attacked). The reason for this may be that δ is also a function of the polarity and hydrogen-bonding capacity of the liquid. Thus, solvents should also be classified according to polarity, and if a true measure of the solvent resistance of a polymer is to be obtained, it should be tested with different classes of solvents. It appears,

¹The data in these tables were collected from various sources by D. Lawson or directly measured by S. P. Vango of JPL.

Table 3. Comparison of solubility parameters and resistance of rubbers to N₂H₄, N₂O₄, and 50/50 UDMH/N₂H₄

Polymer	δ , (cal/cm ³) ^{1/2}	N ₂ H ₄	N ₂ O ₄		50/50 UDMH/N ₂ H ₄	
		Swelling after RT ^b for 3 days; appearance after vacuum drying for 60 hr	Short-term exposure ^a	Long-term exposure	Short-term exposure	Long-term exposure
Poly(isobutylene)	8.1	0.7%; unaffected	70–80°F for 2 hr; swells 60%; liquefied in 16 hr ^c			
Butyl rubber (resin cure)	~8.1		RT ^b for 2 hr; about 60% swell			
Natural rubber (crepe)	8.35	17%; color change from cream to white	70–80°F for 30 sec; broke up RT for 16 hr; liquefied ^c			
Poly(butadiene) rubber	8.45	0%; unaffected in some cases; precipitate extracted in others (effect of different curing agents)	RT for 16 hr; decomposed ^c		160°F for 1 day; precipitate extracted. Swelling not reported	160°F for 30 days; up to 30% swell, 10–80% loss of tensile strength depending on formulation
Styrene-butadiene (23.5% styrene) rubber	8.60	7%; antioxidant dissolved	RT for 16 hr; liquefied ^c			
Poly(styrene)	9.2	0%; no change	RT for 3 hr; dark liquid ^c			
Neoprene rubber, GNA	9.25	20% swell; no change	70–80°F for 4 hr; decomposed RT for 16 hr; decomposed (dissolved?) ^c		70–80°F for 2 days; softens 55–60°F for 30 days; swells, plasticizer extracted	70–80°F for 9 days; softens
Thiokol	9.0–9.4		RT for 16 hr; liquefied ^c			
Buna N	9.4–9.6	7%; some reaction	55–60°F; dissolved < 1 day RT for 16 hr; decomposed ^c		70–80°F for 1 day; results not clear	
Poly(vinyl chloride), plasticized				55–60°F for 30 days; plasticizer is extracted 55–60°F for 90 days; softens 160°F for 1 day; no change 160°F for 7 days; crumbles	70–80°F for 1 day; discolored, softened	
Poly(vinyl chloride), unplasticized	9.6	10%; changed from white to yellow	RT for 16 hr; changed color ^c	70–80°F for 42 days; hardens slightly ^c		

^a Liquid phase exposure, except where noted.

^b RT means room temperature.

^c Gas phase exposure.

Table 3. (contd)

Polymer	δ , (cal/cm ³) ^{1/2}	N ₂ H	N ₂ O ₄		50/50 UDMH/N ₂ H	
		Swelling after RT ^b for 3 days; appearance after vacuum drying for 60 hr	Short-term exposure ^a	Long-term exposure	Short-term exposure	Long-term exposure
Nitroso rubber	5.2	Reacts	70–80°F for 7 days: swells 50–175%, depending on formulation. Elastomeric properties degraded			
Viton A	9.3	Reacts	55–60°F for 1 day; swells	70–80°F for 30 days; decomposes		
Viton B		Reacts	70–80°F for 1 day; swells, then shrinks	55–60°F for 30 days; swells		

from a cursory glance at the literature, that this has not been done for nitroso rubbers, nor have N₂H₄, UDMH, N₂O₄, or diborane been evaluated as to their polarity class. This ought to be done for a better understanding of the mode of attack by these liquids on candidate bladder materials.

Teflon is a material whose δ value is also very low, 6.2 (Ref. 6). It is also crystalline, which ought to hinder diffusion; the combination of these two factors ought to impart excellent properties to it. However, Teflon products are formed by sintering a powder. Unfortunately the interstices of such sintered materials never close completely, leaving pores which cause the high permeability observed.

It has, therefore, been suggested that simple plugging of the pores would reduce the permeability. A surface plugging, obtained by wiping on a film of silicone grease, has not been found to reduce the permeability,² though a silicone would not be expected to impede the diffusion materially. A more effective way of plugging the pores might be to precipitate a material in the pores, just as early osmometer membranes were made by precipitating potassium ferricyanide in clay cups — the two reactants were placed on either side of the cup, they diffused through it and reacted to form a precipitate when they met. The precipitate then became the semipermeable membrane. By leaving the cup in the reactants for long periods of time, the membrane could be made quite impenetrable. This may not be practicable in the present case, since the membrane would have to be semiflexible.

²Measurements by S. P. Vango, JPL.

B. Speculation on the Nature of the Virtually Crosslinked Block Copolymers, R. F. Fedors

1. Introduction

Recently a very interesting class of elastomeric block copolymers composed of alternate segments of styrene and butadiene has been introduced commercially.³ The outstanding feature of these materials depends on the fact that in the absence of any chemical crosslinking, they are capable of mimicking, in a certain temperature range, the behavior of typical chemically crosslinked elastomers. This effect will be described by the term "virtual crosslinking." These materials can be processed and fabricated (e.g., molded, extruded, etc.) at elevated temperatures on normal rubber machinery in the usual fashion. As the temperature is reduced, after the fabrication step, a temperature is reached below which the polymer will function as a virtually crosslinked material.

These polymers are not unique in their ability to function as virtually crosslinked elastomers, plasticized poly(vinyl chloride) (Ref. 6), to cite an example, also behaves in this manner. However, the block copolymers would appear to be of special interest because of their possible unique versatility, i.e., the possibility of varying both the composition and structure of the block segments. It will be evident from this short introduction, that the block copolymer has wide possible application including perhaps that of a binder material for solid propellant (SPS 37-14, Vol. IV, p. 107). In addition, the mere existence of the virtual crosslink effect is of intense interest

³Shell Chemical Co., Thermolastic materials.

in itself, both from a theoretical and experimental standpoint.

Very little information has been released concerning the composition or structure of these block copolymers, and so no mechanism has as yet been published to account for the virtual crosslink effect. For these reasons, it was thought to be of interest to present here some preliminary comments on a possible model for the virtual crosslink effect and some of its consequences.

2. Requirements for the Virtual Crosslink Effect

Although little data have been published, it is known that the commercial polymers are triblocks of the form ABA where A denotes a segment having a relatively high glass transition temperature T_g (such as styrene), and B denotes a segment having a relatively low T_g value (such as butadiene).

An idea of the mechanism of the virtual crosslink effect for these materials may be obtained by considering the nature of the processes occurring during fabrication. When the processing temperature is above T_g of segment A, and thus automatically above T_g of the B segment also, the polymer will flow under stress in a manner not unlike that to be expected for a mixture of the corresponding homopolymers.

Furthermore, if the A and B segments are compatible or mutually soluble, the block copolymer will consist of a single thermodynamic phase over the temperature range of interest. On the other hand, if A and B segments are incompatible or mutually insoluble, a two-phase system will result in which the A and B segments will tend to aggregate to form domains whose size will depend to a first approximation on molecular weight. It may be noted here that polymer compatibility is a function of molecular weight, temperature, and the extent of intermolecular interaction. It turns out that polymer-polymer insolubility is far more common than is solubility (Ref. 7).

As the temperature is decreased to values below the expected T_g of segment A, in the case of a single phase, no abrupt changes in properties are expected, since the single phase has only one T_g value. This kind of polymer will have the ability to flow at all temperatures down to the T_g of the mixture or single phase, a value which will be intermediate between the T_g values of the components. On this basis, compatible segments are not predicted to lead to the occurrence of virtual crosslinking. It is of interest here that another elastomer composed of 25 mole % styrene and the

remainder of butadiene and described as a block copolymer does not display virtual crosslinking (Ref. 8). Evidently the segment lengths are too short to permit mutual insolubility.

However, the case of the two-phase (or more generally, multi-phase) system will be characterized by two T_g values (or multiple T_g values). In this situation, as the temperature is reduced to a value near T_g of the A segment, these segments will undergo a second-order transition and will now exist as a high modulus glass. For this temperature and temperatures down to T_g of the B segment, these glassy domains are predicted to function as crosslink sites for B segments in polymers of the type ABA. That is, since each B segment is capped at each end by segments which are in the glassy state, the possibility of these domains functioning as crosslink sites is present. The "functionality" of the crosslink will depend on the domain size. Thus, the functionality will be numerically equal to the number of A segments present in the domain. To the extent that the possibility exists for varying the A domain size either by mechanical or thermal treatment, then it should be possible to vary crosslink functionality.

It is thus predicted that diblocks of the type AB and inverted triblocks of the type BAB cannot function as virtually crosslinked elastomers because in each of these cases, only one end of the B segment is attached to a possible crosslink site, i.e., to the glass-forming A segment. Support for this contention is provided by the fact that elastomeric materials prepared from mechanically blending of high molecular weight homopolymers of butadiene and styrene do not possess the virtual crosslink property.

3. Filler Effects

Since incompatibility implies that the number of contacts between A and B segments will tend to be a minimum, it is expected that the A and B segments will tend to exist in A-rich and B-rich domains. The size, geometric shape and number of these domains will be a strong function of both the mechanical and thermal history. For temperatures below T_g of the A segment, however, these domains should be relatively insensitive to temperature, since any change in size would necessarily depend on diffusion of A in the glassy state, which is not likely to occur in reasonable time periods. Because of the great difference in the modulus of a glass as compared to the modulus of an elastomer, most of the deformation in the temperature range for which the virtual crosslink effect is present, will take place in the B segment domains. Thus, the A domains should function in a manner similar to that of small-particle-size particulate fillers such as carbon black. These

latter filler effects should not be observable in the non-crosslinkable *AB*-type and the inverted *BAB*-type block copolymers, however, and should be manifested as an increase in viscosity. Thus, the glass domains are thought to perform two independent functions: (1) they act as virtual crosslinks for the *B* segments, and (2) they behave as small, nonagglomerated particles.

4. Criteria for Block Segments

The segment properties for copolymers of the type *ABA* which were presumed to influence the behavior of these materials have been discussed in a qualitative fashion. In what follows, an attempt will be made to discuss in a more quantitative manner several of the variables which determine the behavior of the system, such as segment compatibility, molecular weight and volume ratios of *A* to *B* segments.

5. Conditions Required for Insolubility

In order to study some of the variables which determine solubility, it is assumed that the liquid lattice theory developed by Flory and Huggins (Ref. 7) is valid. It is recognized that although the theory is not, in general, in quantitative accord with experimental results, it is also true that the theory provides a satisfactory qualitative explanation for the behavior of polymer solutions. Use of more elaborate theory, while narrowing the divergence between theory and experiment, also loses simplicity and hence is not warranted at the time.

The change in chemical potential, $\Delta\mu_1$, of component 1 in solution relative to the pure component can be written as (Ref. 7):

$$\Delta\mu_1 = RT \left[\ln(1 - v_2) + \left(1 - \frac{V_1}{V_2}\right) v_2 + \chi_{12} v_2^2 \right] \quad (1)$$

and likewise for component 2,

$$\Delta\mu_2 = RT \left[\ln v_2 + \left(1 - \frac{V_1}{V_2}\right) (1 - v_2) + \chi_{12} \frac{V_2}{V_1} (1 - v_2)^2 \right] \quad (2)$$

where R is the gas constant, T the absolute temperature, v_2 is the volume fraction of component 2, V_1 is the molar volume of component 1, V_2 is the molar volume of component 2 and χ_{12} is the interaction coefficient between components 1 and 2. This latter quantity is related to the heat of mixing, i.e., the increment of energy associated with the formation of intermolecular contacts between

components 1 and 2 in solution relative to the pure components. In using Eq. (1) and (2), the fact that component 1 and component 2 belong to the same molecule is ignored.

An inspection of Eq. (1) and (2) demonstrates that the effect of chemical structure of the polymer influences $\Delta\mu_1$, and $\Delta\mu_2$ only through the quantity χ_{12} , which can be written as (Ref. 9):

$$\chi_{12} = \frac{M_1}{\rho_1 RT} (\delta_1 - \delta_2)^2 = \frac{M_1 (\Delta\delta)^2}{\rho_1 RT} \quad (3)$$

where δ_1 and δ_2 are the cohesive energy densities of components 1 and 2 respectively, ρ_1 and ρ_2 are the densities of components 1 and 2 respectively, and M_1 is the molecular weight of component 1. The equation shows that χ_{12} is directly proportional to the molecular weight of component 1 and to the square of the cohesive energy difference. The δ value is a convenient measure for the intensity of intermolecular interaction in the pure component and as such can be obtained in several ways, for example, for low molecular weight materials from their heats of vaporizations (Ref. 10). Several compilations of values for both low molecular weight and high molecular weight materials are available (Refs. 10, 11, and 12). There is also a useful method due to Small for estimating cohesive energy densities of polymers from a table of additive constants requiring only a knowledge of the polymer structure (Ref. 9). In any event, a knowledge of δ values along with Eq. (1), (2), and (3) are sufficient to completely determine the phase relationships for a two-component system. The predicted phase diagram for a two-component system is shown in Fig. 2 in a plot of the reciprocal χ_{12} versus v_1 , for several values of molar ratio, V_1/V_2 . It is evident that the curves for fixed values of V_1/V_2 become increasingly asymmetrical as the ratio increases, i.e., as the disparity in the molar volumes of the two components increases. At a fixed difference in the cohesive energy densities, $\Delta\delta$, decreasing the molecular weight M_1 increases polymer compatibility, while at constant molecular weight, M_1 , compatibility increases as $\Delta\delta$ decreases, i.e., as the components become more similar in chemical structure.

It is evident from Fig. 2 that absolute insolubility will only occur when either M_1 or $\Delta\delta$ become infinite. However, as a practical matter, it is probable that some small measure of solubility could be tolerated while still maintaining reasonable mechanical properties. When $RT\rho_1/M_1(\Delta\delta)^2$ has a value of about 0.1 or less the volume fraction of the *A* segment soluble in the *B* segment will be 0.01 or less and if it is assumed that this measure of solubility is negligible, then values of approximate minimum molecular

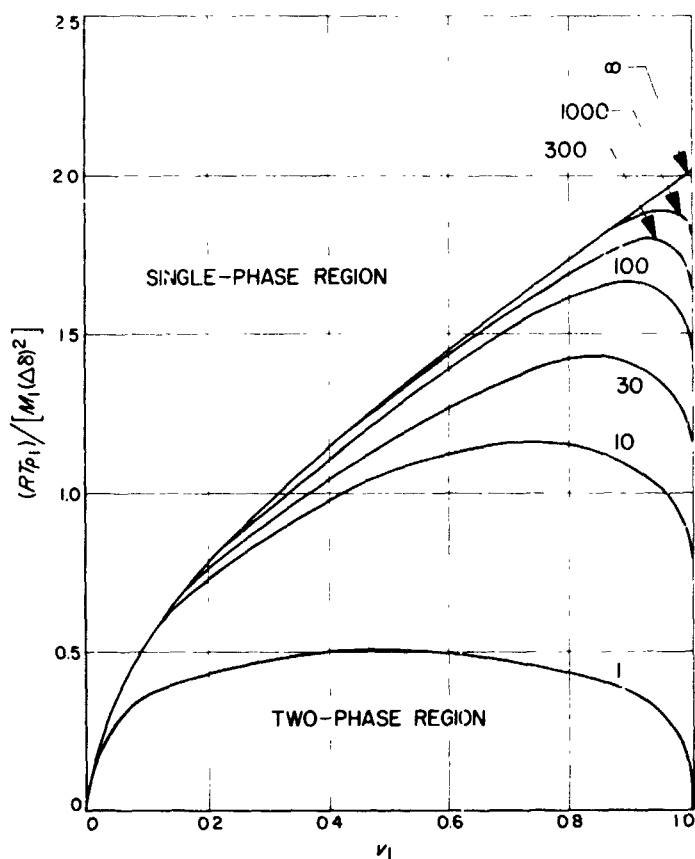


Fig. 2. Phase diagram for a two-component system. Numbers correspond to the ratio V_1/V_2

weights for the segments can be calculated. As a practical example, consider segment A to be styrene and segment B to be butadiene, and take styrene as component 1 and butadiene as component 2. For styrene, $\delta_1 = 8.83$ and for butadiene, $\delta_2 = 8.44$ which leads to a value of $\Delta\delta = 0.39$ (Ref. 10). Using Eq. (3), a minimum estimate for M_1 is obtained from,

$$M_1 (\text{minimum}) \approx \frac{(1.04)(2)(373)}{(0.15)(0.1)} = 5000 \quad (4)$$

In Eq. (4) T was set equal to 373°K , the approximate T_g for polystyrene and ρ_1 was taken as 1.04 g/cm^3 . The minimum value of $M_1 = 5000$ implies that the minimum molecular weight of each styrene segment is of the order of 2500 for an ABA-type block copolymer. An estimate of the minimum molecular weight for the butadiene segment obtained in an analogous manner, is about 6000. Hence, the predicted lowest molecular weight for the ABA system which guarantees negligible solubility is $A = 2500$ and $B = 6000$. It should be pointed out that the minimum molecular weight numbers are subjected to considerable

uncertainty because the individual δ values are not precisely known.

If mutual insolubility were the only factor involved in determining the suitability of a given monomer pair, then Eq. (4) would provide sufficient information. However, also to be considered is the requirement of a sufficiently high T_g for segment A so that ABA triblock will function as a virtually crosslinked elastomer in a useful temperature range.

6. Influence of Molecular Weight on T_g

In Fig. 3 are shown data for the glass transition temperature of fractionated polystyrene as a function of the molecular weight. The filled circles represent data from Ref. 13 while the unfilled circles represent data from Ref. 14. It is evident from Fig. 3 that although there is a very rapid increase in T_g with molecular weight in the low molecular weight range, i.e., roughly for molecular weights up to 10 to 12,000, for higher molecular weights, the relative increase in T_g is rather small. For example, with a molecular weight of 12,000, $T_g = 89^\circ\text{C}$, whereas for a molecular weight of 40,000, $T_g = 97^\circ\text{C}$ —an increase in only 8°C for a three-fold increase in molecular weight. In the case of polystyrene homopolymer, above a molecular weight of about 40,000 the bulk viscosity increases as the 3.4 power of molecular weight (Ref. 15). Since bulk viscosity is an important processing parameter, with lower bulk viscosities implying lower processing temperatures, the most suitable molecular weight would be the lowest

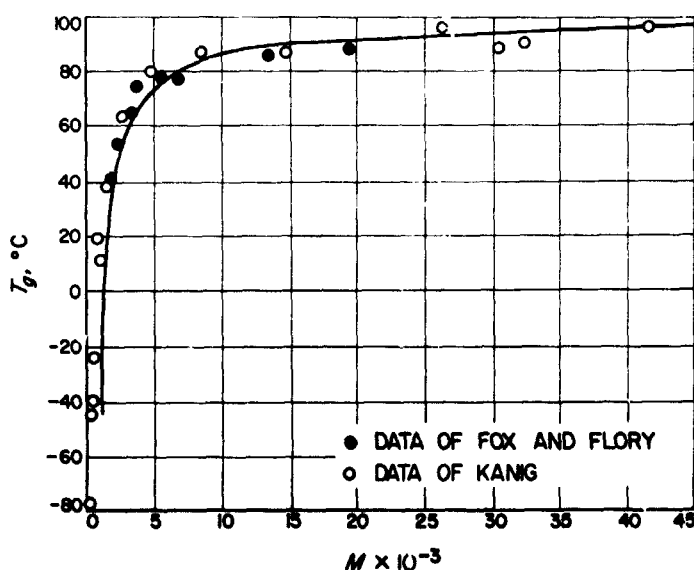


Fig. 3. Dependence of glass transition temperature on molecular weight for fractionated polystyrene

value which provides a sufficiently high T_g . For the case polystyrene, a molecular weight of 12,000 and a T_g in the undeformed state of 89°C would appear suitable. This molecular weight is to be contrasted to a minimum molecular weight value calculated on the basis of solubility of 2500 which would correspond to a T_g value of about 50°C. A gain of about 40°C in T_g can be obtained by increasing molecular weight from 2500 to 12,000.

For other polymer types, the necessary T_g versus molecular weight data may not be as extensive as is the data on polystyrene. In this case, estimates for T_g can be obtained by using any one of several available relationships which relate T_g to molecular weight. For example, using free volume considerations, Bueche (Ref. 16) has derived the following equation:

$$T_g = T_g(\infty) - \frac{K}{M} \quad (5)$$

where $T_g(\infty)$ is the glass transition temperature for polymer of infinite molecular weight, and K is a constant for a given polymer. If T_g is known for two molecular weights, K and $T_g(\infty)$ can be evaluated and the results used to calculate T_g for other molecular weight values. Eq. (5) is not expected to be valid for low values of molecular weight. As an indication of the usefulness of the equation, the full curve shown in Fig. 3 is the prediction of Eq. (5) with $K = 10^5$ moles/g and for $M > 4000$, the fit to the experimental data is excellent.

In instances where bulk viscosity plays a decisive role, a decrease in viscosity can be obtained by employing a glass-former having a higher T_g value. In this case, a given T_g value, say 90°C, can be obtained using a lower molecular weight segment. For example, $T_g(\infty)$ for α -methylstyrene is about 170°C. Assuming Eq. (5) holds using the same value for K , the following expression can be obtained:

$$T_{g1}(\infty) - T_{g2}(\infty) = K \left(\frac{1}{M_1} - \frac{1}{M_2} \right) \quad (6)$$

Using the appropriate values, i.e., $T_{g1}(\infty) = 100^\circ\text{C}$, $T_{g2}(\infty) = 170^\circ\text{C}$, and $M_1 = 12,000$, M_2 , the molecular weight of the equivalent α -methylstyrene segment, turns out to be roughly 2000, or a factor of 6 lower than the value obtained using polystyrene. There is a limit to how far the molecular weight can be reduced by this procedure since in any case, the molecular weight must be

at least as high as the minimum value necessary to ensure insolubility. As will be indicated below, a lower value of molecular weight for the A segment implies a lower value for the B segment also.

7. Influence of Strain on T_g

Another important factor which bears on the question of the appropriate T_g value for the glassy segment is the question of the effect of strain on T_g . Based on free volume considerations, Ferry has derived an equation for the shift in time scale due to an imposed strain (Ref. 17):

$$\log a_\epsilon = - \frac{\frac{\epsilon}{2.303f_0}}{\frac{\beta f_0}{\beta(1-2\mu)} + \epsilon} \quad (7)$$

where a_ϵ is the shift factor, ϵ is the strain, f_0 is the fractional free volume at $\epsilon = 0$, β_f is the compressibility of free volume, β is the total compressibility, and μ is Poisson's ratio. Since μ is less than or equal to $1/2$, Eq. (7) predicts that an imposed strain will always decrease the effective T_g . In order to estimate the reduction in T_g , a_ϵ is set to equal the time-temperature shift factor a_T , given by:

$$\log a_T = - \frac{\frac{T - T_g}{2.303f_g}}{\frac{f_g}{\alpha_f} + T - T_g} \quad (8)$$

Setting $\log a_\epsilon = \log a_T$, there is obtained:

$$\left(\frac{\beta_f}{\beta} \right) \frac{f_0^2}{(1-2\mu)\epsilon} + f_0 = \frac{f_g^2}{\alpha_f(T - T_g)} + f_g \quad (9)$$

where f_g is the free volume at T_g when $\epsilon = 0$, and α_f is the expansion coefficient of the free volume. Assuming $(\beta_f/\beta) \approx 1$, which implies that compressibility is due only to the variation of free volume with pressure, and since the temperature range of interest is $T \approx T_g$, f_0 can be taken equal to f_g , which yields:

$$-\Delta T_g \approx \frac{(1-2\mu)\epsilon}{\alpha_f} \quad (10)$$

For glassy polystyrene, $\mu = 0.33$ and $\alpha_1 \approx 4 \times 10^{-4}$ per $^{\circ}\text{C}$ (Ref. 18), hence,

$$-\Delta T_g = 850 \epsilon \quad (11)$$

which predicts a decrease in T_g of 8°C for each 1% strain imposed on polystyrene. Although the small strain modulus of a glass is roughly 10^4 to 10^5 times greater than the small strain modulus of an elastomer, it is not inconceivable that the glass would undergo strains of a few percent when the overall strains on the system are of the order of 1000%. This is especially true if the glass domains behave as filler particles, because in that capacity the domains could function as stress concentrators. Hence, strain could cause a reduction of about 20 to 30°C in the effective T_g of the glass. This consideration would imply that the T_g of the glassy segment must be designed to be about 20 to 30°C higher than the maximum temperature for which the polymer is designed to operate. Thus, for the case of polystyrene, with the molecular weight chosen as 12,000, the maximum temperature for which the polymer will function as a virtually crosslinked elastomer is 60 to 70°C .

8. Domains as Filler Particles—Molecular Weight Effects

The volume fraction of segment A, ϕ_A , can be shown to be:

$$\phi_A = \frac{2M_A \rho_B}{2M_A \rho_B + M_B \rho_A} \quad (12)$$

If segment A is insoluble in segment B, then ϕ_A should represent the volume fraction of "filler." If this analogy is valid, then a virtually crosslinked block copolymer can be compared in a formal fashion to "bound rubber," which is an insoluble gel composed of carbon black and rubber which is produced when active carbon blacks are mixed into rubber under the influence of high shearing forces. There is much evidence to show that in bound rubber the polymer chains are attached to the carbon black particle by means of chemical bonds (Ref. 19), and in this sense the carbon black particle might be considered as part of the polymer chain.

If the glassy domains function as filler in a fashion similar to carbon black, then experience with vulcanized rubber shows that the optimum volume fraction of filler should be about 0.25. Assuming this to be the case, then it is easy to demonstrate that the molecular weights of the A and B segments cannot be varied indiscriminately

while still maintaining useful elastomeric properties for the polymer. Eq. (12) shows that once ϕ_A is fixed, this automatically provides the relationship between M_A and M_B . For example, in the case of polystyrene, $M_A = 12,000$, $\rho_A = 1.04$, and $\rho_B = 0.96$ and taking $\phi_A = 0.25$, M_B is calculated to be about 83,000. Thus the total molecular weight of the ABA molecule would be about 110,000. For the case of α -methylstyrene, assuming $M_A = 3000$, the minimum molecular weight required to ensure insolubility, then M_B is calculated to be 21,000 or about 30,000 for the ABA molecule. It might be expected that a block copolymer with a molecular weight of 30,000 would be processible at far lower temperatures than one with a molecular weight of 110,000.

In this connection, Baranwal (Ref. 20) studied the effect of filler particle size on the stress-strain behavior of an SBR rubber using spherical polystyrene particles as filler. The particle sizes ranged from 357 to 1430 Å. He was able to show that both tensile strength and ultimate elongation increased with increasing volume fraction of polystyrene filler. Volume fractions of polystyrene in the range 0 to 0.25 were investigated. He was also able to study the effect of chemically linking the polystyrene filler to the rubber molecule. Although it is not clear from his data what effect chemically linking of the filler had on either the tensile strength or the ultimate elongation, nevertheless, the study shows that polystyrene can function as a "reinforcing" filler.

9. Domains as Filler Particles—Effect of Domain Size

It is of interest to attempt to determine an approximate size for the glass domain. In each phase, the chains or segments will tend to assume their unperturbed dimensions, for which the root-mean-square end-to-end distance $(\bar{r}_0^2)^{1/2}$ may be used as an appropriate measure of the size of a random coiling polymer chain. In using this measure of coil size, the tacit assumption is that the A and B segments behave as separate molecules. The values of $(\bar{r}_0^2)^{1/2}$ can be obtained experimentally in several ways, for example, from intrinsic viscosity measurements at the theta temperature. For polystyrene, $(\bar{r}_0^2)^{1/2} \approx 0.65 M_A^{1/2} \text{ Å}$ and for polybutadiene, $(\bar{r}_0^2)^{1/2} \approx M_B^{1/2} \text{ Å}$ (Ref. 21). These are the end-to-end chain distances to be expected in the bulk phase, i.e., in the absence of interaction between A and B segments. In the case of polystyrene, it will be assumed that this end-to-end distance, $(\bar{r}_0^2)^{1/2} \approx 0.65 M_A^{1/2} \text{ Å}$ characterizes the polystyrene coil at temperatures arbitrarily close to T_g . It has been demonstrated by Flory (Ref. 22) that chain segments of a randomly coiled molecule extend over dimensions equal to twice the $(\bar{r}_0^2)^{1/2}$ value.

Hence, the effective diameter of a coil can be taken as $2(\bar{r}_0^2)^{1/2}$. In the case of the block copolymer, if the glass domain is spherical in shape, then the maximum diameter should be approximately $4(\bar{r}_0^2)^{1/2} = 4(0.65)(12,000)^{1/2} \text{ \AA} \approx 300 \text{ \AA}$. This value for particle diameter is the same order of magnitude as the particle diameter for commercially available carbon blacks. For example, SAF black, diameter = 140 to 170 \AA; HAF black, 260 to 350 \AA in diameter; and FEF, 310 to 580 \AA in diameter.

In addition to the formation of spherical domains, it is likely that sheet-like or plate-like domains are also present. In this case, the maximum thickness of the sheet or plate will be roughly $4(\bar{r}_0^2)^{1/2} \approx 300 \text{ \AA}$, as was the case with the spherical domain. However, for the sheet, growth in the lateral directions should be possible so that lateral dimensions may be much larger than the thickness of 300 \AA. It is expected that there is likely to be a distribution in both size and geometrical shape for the glass domains. There will be a tendency to make the surface free energy of the domains a minimum which implies that the domains will tend to be as large as possible, subject to the condition that the domain be essentially a pure phase.

10. Domain Functionality

If the size of the domain is known, then the functionality of the crosslink can be obtained. For the case of the spherical domain,

$$f = \frac{V_{\text{domain}}}{V_{\text{segment}}} = \frac{\frac{4}{3} \pi [2(\bar{r}_0^2)^{1/2}]^3}{\frac{M_A}{N \rho_A}} = 57.6 M^{1/2} \quad (13)$$

or $f \approx 600$ for polystyrene having a molecular weight of 12,000. In Eq. (13), N is Avogadro's number. It is interesting to note that f is proportional to the square root of the molecular weight. For typical chemically crosslinked vulcanizates such as natural rubber cured with sulfur, the crosslink functionality is thought to be about 4. On this basis the calculated f value for the glass domain is exceptionally high, and this fact may have bearing on the behavior of the block copolymers. For example, it is not known what effect both a crosslink of finite size and one of high functionality have on mechanical properties.

In the above discussion it has been tacitly assumed that the segments were monodisperse, i.e., of uniform

molecular weight. In case this is not valid, i.e., the molecular weight is not uniform, then the block copolymer is expected to exhibit poorer mechanical properties. There are three cases to consider: (1) if the B segments were uniform but the A were not, then the lower molecular weight A segments, being soluble in the B segment, could not function as crosslink sites, and hence the fraction of the polymer which could support a load would be reduced; (2) if the A segments were uniform but the B were not, then the lower molecular weight B segments, being soluble in the A segment, would reduce the T_g of the A domains and thus reduce the maximum temperature for which the block would function as a crosslinked system; (3) if both the A and B segments were not uniform in molecular weight, then the above two factors would be operative simultaneously.

11. Application of Propellant Binders

The fact that properly designed block copolymers do not have to be chemically crosslinked make these materials of special interest for application as a binder material. Since the glassy domains function as filler, it is evident that for binder applications, ϕ_A should be as low as possible. However, the molecular weight of segment A is essentially fixed by the requirements of insolubility and sufficiently high T_g . According to Eq. (12), at fixed M_A the quantity ϕ_A can be decreased only by increasing M_B , the molecular weight of the B segment. However, increasing M_B at fixed M_A produces an increase in the weight of the ABA molecule which will tend to increase processing difficulties.

It can be shown that the relationship between the true volume fraction of filler ϕ_T , which assumes that both the glass domains and added oxidizer function as filler, and the apparent volume fraction of filler ϕ_{app} , which assumes that added oxidizer is the only filler present, can be written as:

$$\phi_T = \phi_{app}(1 - \phi_A) + \phi_A \quad (14)$$

Using Eq. (12) to express ϕ_A as a function of segment size, Eq. (14) can be written as

$$\phi_T = \phi_{app} + (1 - \phi_{app}) \frac{2M_A \rho_B}{2M_A \rho_B + M_B \rho_A} \quad (15)$$

Eq. (15) shows that ϕ_T is always greater than ϕ_{app} . (The two will be equal only when $M_A = 0$.) Furthermore, if ϕ_{app} is made equal to or approximately equal to ϕ_{max} , i.e., the maximum volume fraction of filler which the

binder can accommodate and still maintain a two-phase system. Then since $\phi_T > \phi_{mix}$, the system will necessarily be a three-phase system (binder, filler, and voids) and dewetting exists in the composite even before any deformation is allowed to occur.

If ϕ_{mix} is assumed to be about 0.70, and using $M_A = 12,000$ and $M_B = 83,000$, then Eq. (15) predicts that only 0.60 volume fraction of oxidizer can be added and still maintain a two-phase system.

12. Summary

A model for the virtual crosslink effect in triblocks of the type ABA, where A is a segment having a relatively high T_g value, and B is a segment having a relatively low T_g value has been presented. It is predicted that at least two requirements are necessary in order for the block copolymer to behave as a chemically vulcanized elastomer: (1) that the A and B segments be mutually insoluble, and (2) that the A segments have a higher T_g value than the maximum temperature at which the material will be expected to function. The size of the glass domain has been discussed along with the suggestion that the glass domains fulfill two functions: (1) as crosslinks and (2) as filler particles.

C. Use of the Trifluoromethyl Group as an F^{19} NMR Probe in Polymeric Systems, D. D. Lawson and J. D. Ingham

Since the chemical reactivity and mechanical behavior of polymers are determined by their molecular structure, methods of readily determining this structure, particularly for the most reactive sites of the polymer, are required. For prepolymers applicable as solid propellant or spacecraft materials the most important reactive sites are the end-groups, which influence curing and degradative reactions, and any chain or sidechain unsaturation, particularly in polybutadienes, which affects mechanical properties, processing, and stability. Although high-resolution proton magnetic resonance spectroscopy is applicable to the structure determination of many organic compounds, the multiplicity of protons in the different structural environments in prepolymers often results in extremely complex spectra, usually with overlapping signals that are difficult or impossible to interpret.

The methods described in this report involve the chemical insertion of a moiety containing fluorine at the relevant reactive sites in a polymeric system. The dual

effect is to avoid the broad signals that are normally observed in proton polymer spectra and to gain the increased chemical shift range of fluorine resonances. Although the chemical shifts, or positions of either proton or fluorine NMR signals, relative to appropriate internal standards, depend on the surrounding magnetic environment and chemical structure, the separation of fluorine resonances is generally greater than corresponding proton signals by a factor of ten or more. The logical NMR probe is the trifluoromethyl group, because it has three equivalent fluorines which generally yield a single narrow line for each structural environment. In previous work we described the introduction of the trifluoromethyl moiety in the form of the trifluoroacetyl group in poly(alkylene oxides) to determine the structure and configuration of terminal hydroxyl groups present (Ref. 23). This has been extended by the use of trifluoromethanesulfonyl chloride (I) which yields the sulfonate esters of the corresponding diols (SPS 37-40, Vol. IV, pp. 93-95). The addition of sulfonyl chlorides to olefinic double bonds is a well-known and interesting reaction that we have also considered as a method for introducing the trifluoromethyl group as a probe for unsaturated systems. Because of the complex products obtained with some model alkenes and (I) it was felt that a probe which yielded simple products was more desirable. It appears that trifluorothioacetic acid (II) reacts with double bonds by direct addition in a relatively straightforward manner to yield derivatives that give F^{19} spectra which are sensitive to their structural environment.

1. Reaction of Trifluoromethanesulfonyl Chloride With Double Bonds

Primarily we have been interested in double bonds associated with poly(alkenes). The use of (I) in the study of model alkenes has yielded F^{19} NMR spectra that are in some cases single lines, but in others are a series of complex spectra. Fig. 4 shows the range of spectra obtained by reacting (I) with a given alkene. There is some evidence that the adducts of (I) with alkenes may be a two or more step process, where the reagent adds to the alkene to give the anti-Markownikoff products, which, on standing at ambient temperatures, rearrange to the Markownikoff-oriented material (Ref. 24). Also, the adducts in some instances tend to eliminate hydrogen chloride to form unsaturated sulfides. Furthermore, it is possible that diastereoisomers are formed that are magnetically nonequivalent and give rise to two lines for each isomer pair. In the reaction of a polybutadiene polymer with (I), as shown in Fig. 5, hydrogen chloride is evolved, with the unsaturated sulfide most likely being

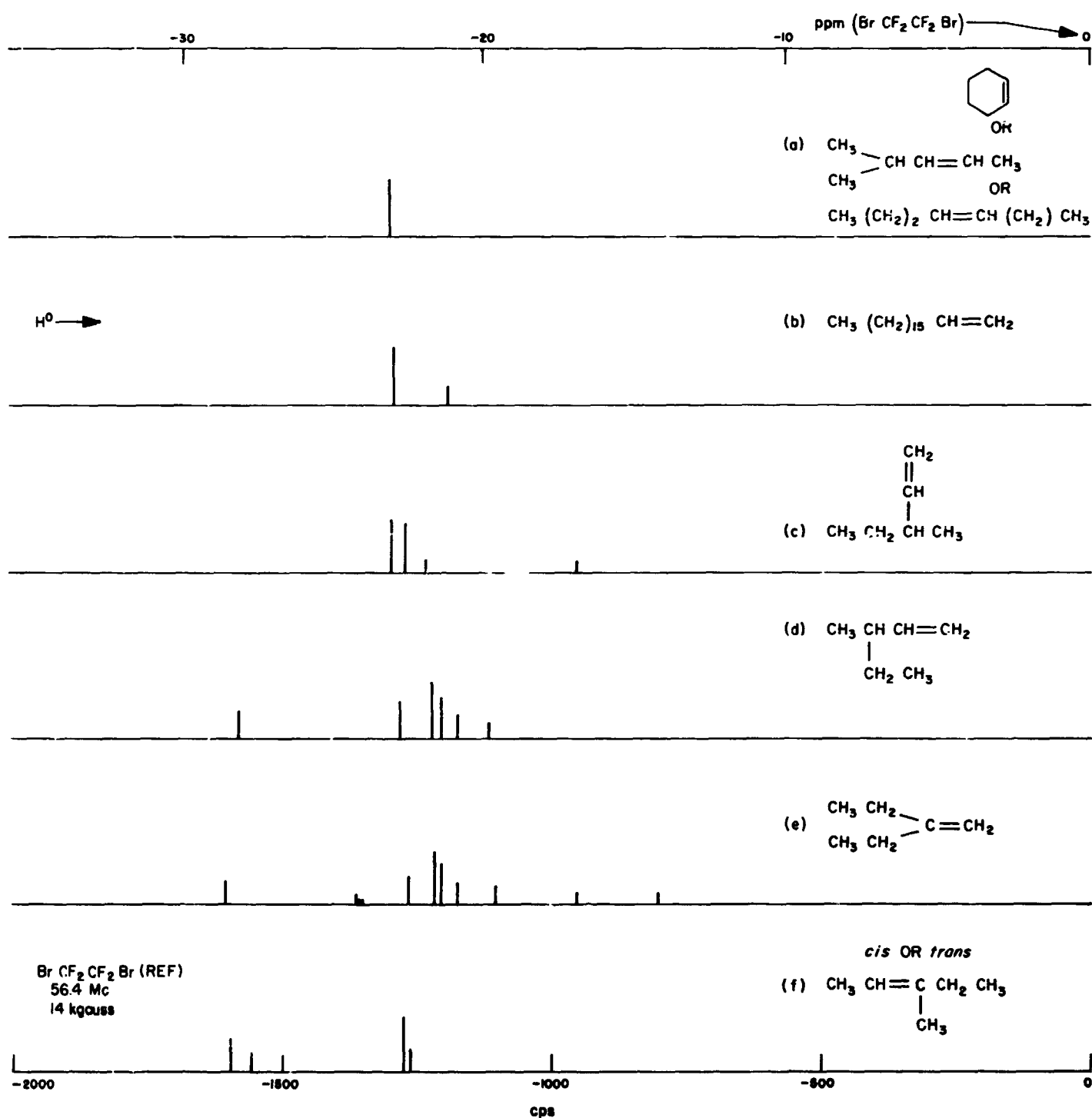


Fig. 4. ¹⁹F NMR spectra of the neat reaction mixture of alkenes and CF₃SCl at ambient temperature

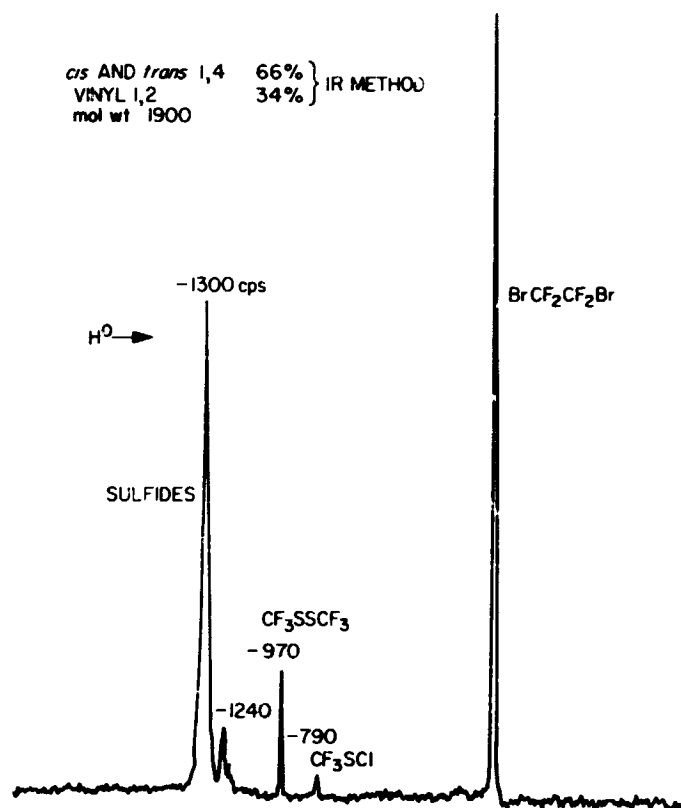


Fig. 5. F^{19} spectra of hydroxyl-terminated polybutadiene reacted with (II)

formed from the pendant vinyl groups. From this spectra the relative concentration of the chain double bonds or pendant vinyl groups in the polymer is not apparent.

In certain situations it may be possible to vary the conditions for reaction of (I) to study the hydroxyl and double bonds simultaneously or successively in the presence of each other. The reaction of (I) with a hydroxyl group is negligible in the absence of a base such as pyridine, and the reaction of the olefinic double bond can be controlled by suitably adjusting the temperature. An example, using 2-octene-4-ol, is shown in Fig. 6. The chemical shifts for the three derivatives are consistent with the observed values given in Fig. 7.

2. Reaction of Trifluorothiolacetic Acid With Double Bond Systems

The complex products that are obtained in the reaction of some alkenes and (I) led us to investigate the use of trifluorothiolacetic acid (II) as a method of introducing a trifluoromethyl probe into an alkene. In reaction 1, the addition of a thiol acid to a double bond is a free radical

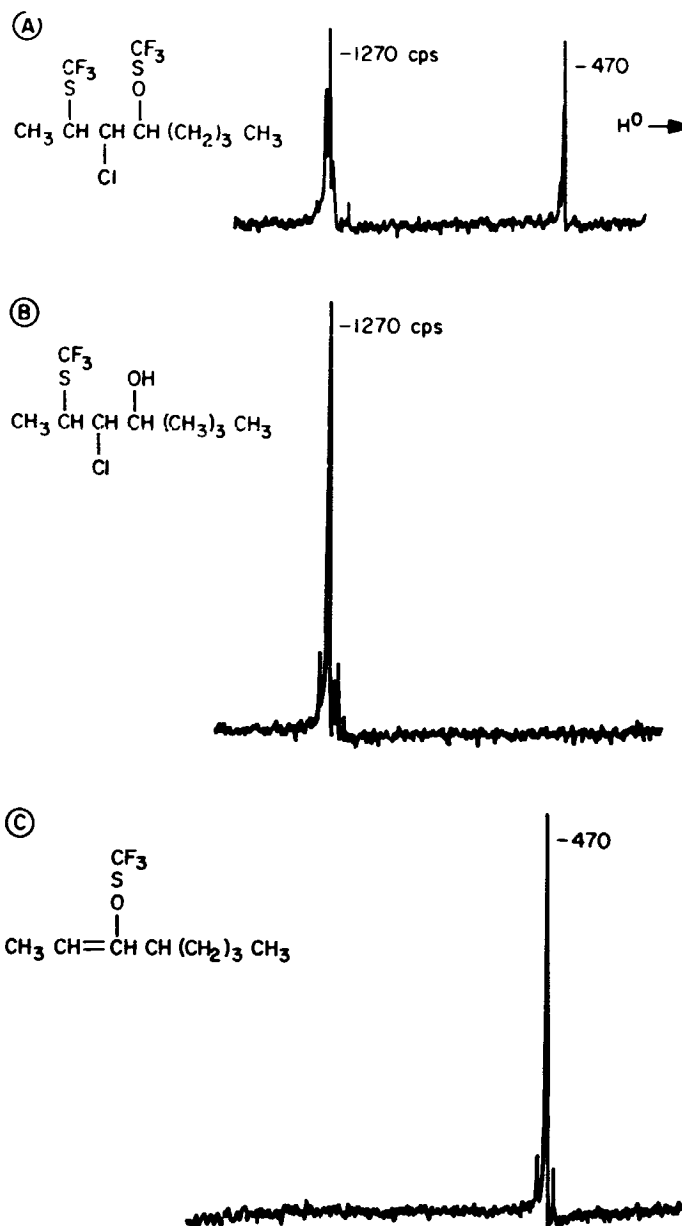
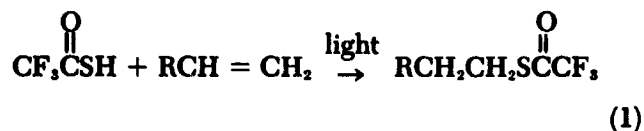


Fig. 6. Steps of reaction of 2-octene-4-ol with trifluoromethanesulfonyl chloride

process and yields products that are anti-Markownikoff-oriented.



In this reaction there is no possibility of the elimination of hydrogen chloride to form the unsaturated sulfides. The chemical shift range of the thioesters of the model

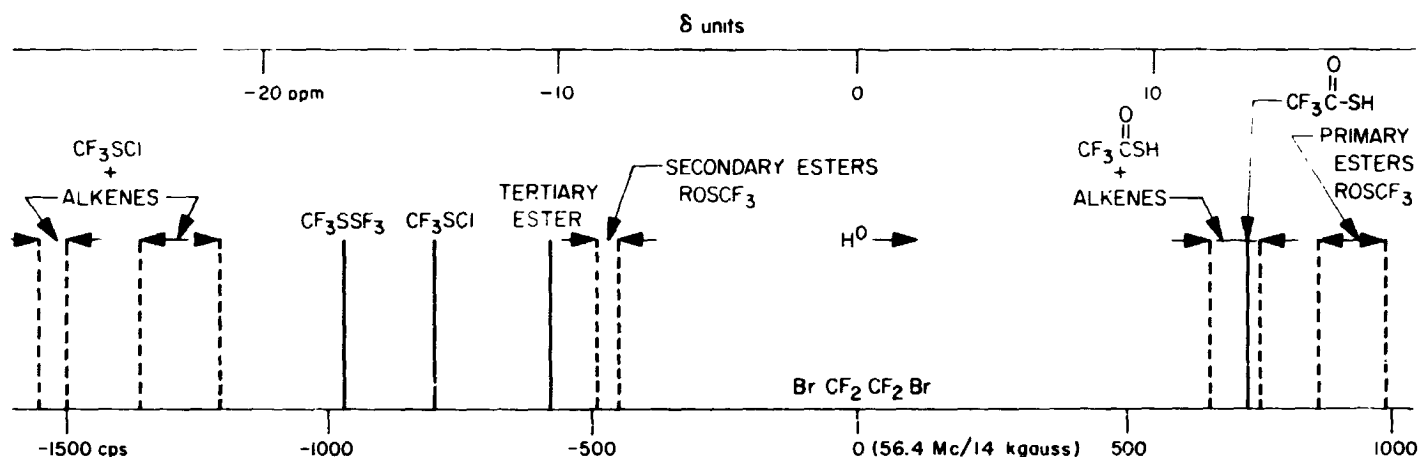


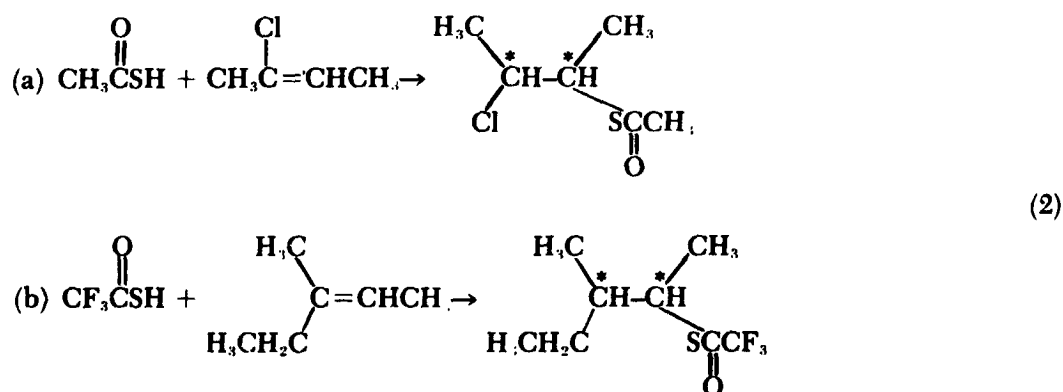
Fig. 7. Summary of chemical shifts of trifluoromethanesulfonyl chloride (I), trifluorothioacetic acid (II), and related derivatives

compounds and polymers is about 130 cps, as shown in Table 4.

In the case of trifluorothioacetic acid (II) reacted with a polybutadiene polymer the relative amounts of vinyl and chain double bonds can be estimated from the spectra as shown in Fig. 8. Apparently the polymer derivatives act as solvents and thus cause the NMR signals to appear at a lower magnetic field than the model compounds. An aromatic ring adjacent to a double bond as in styrene has a marked effect on the F^{19} NMR signal of the thioester derivative, shifting it downfield. It ap-

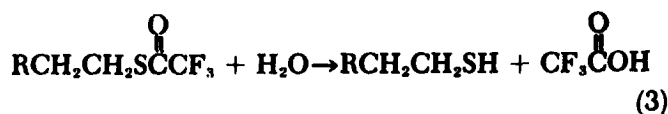
pears that 2,3-dimethyl-2-butene (tetramethyl ethylene) will not react with (I) even when exposed to ultraviolet light for prolonged periods. The failure to react can most likely be attributed to the predominant effect of steric hindrance.

Bordwell, et al., reacted thioacetic acid with *cis* and *trans* 2-chloro-2-butene and showed (reaction 2a) that diastereoisomers were formed (Ref. 25). The reaction of trifluorothioacetic acid with 3-methyl-2-pentene as shown in reaction 2b should yield the threo and erythro adducts in the same manner as 2-chloro-2-butene.



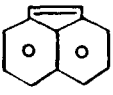
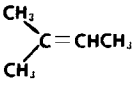
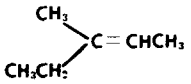
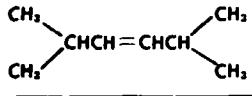
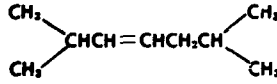
In Fig. 9 the room temperature F^{19} NMR spectra of the reaction mixture shows two thioester peaks that are separated by about 3 cycles. These are most likely the *dl* forms of threo and erythro thioesters (Ref. 26).

The thioesters that are formed from alkenes have a tendency to undergo hydrolysis to yield the mercaptan as shown in reaction 3.



Therefore, in cases where quantitative information is required, the use of water or compounds which can undergo an exchange reaction with the thioester should be avoided.

Table 4. Derivatives of alkenes and polymers with trifluorothioacetic acid (II)

Reactants	Cycles/sec from $\text{BrCF}_2\text{CF}_2\text{BR}$	Comments
$\phi^*\text{C}\equiv\text{C}\phi$	+620 ^b	1 to 1 ratio of $\bar{\text{C}}$ and I
	+660 ^b	Two much smaller lines ~ 10 cps downfield
$\phi\text{CH}=\text{CH}_2$ $\phi\text{CH}=\text{CHCH}_2$	+685 ^b	
$\begin{array}{c} \text{CH}_3 \\ \\ \phi\text{C}=\text{CH}_2 \end{array}$	+695 ^b	
$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$  	+705 ^c	
$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CH}$	+708 ^b	1 to 1 ratio of $\bar{\text{C}}$ and I
$\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$	+712 ^c	
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_2 \end{array}$	+720 ^c	
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_2 \end{array}$	+725 ^c	
CF_3COSH	+738	Neat
	+745 ^c	
	744-746 ^c	3 lines
Cis-polybutadiene (95% 1,4 addition)	+670 ^b	
High vinyl polybutadiene (91% 1,2 addition)	+685 ^b	
Polybutadiene secondary hydroxyl-terminated mol wt ~ 2000 By IR method 66%, 1,4 and 34% 1,2 (vinyl)	+688 ^b +675	About 2-to-1 area ratio (Fig. 8)

^a ϕ = phenyl
^b Benzene solution
^c The neat reaction mixture of 1 mole of (II) and 2 moles of the olefin.

cis AND *trans* 1,4 66%
 VINYL 1,2 34%
 mol wt 1900

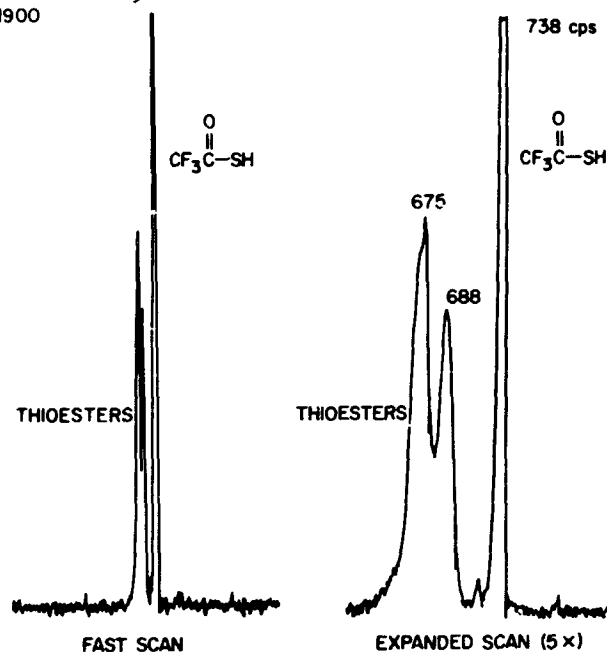


Fig. 8. Spectra of the reaction mixture of trifluorothioacetic acid and a hydroxyl-terminated polybutadiene

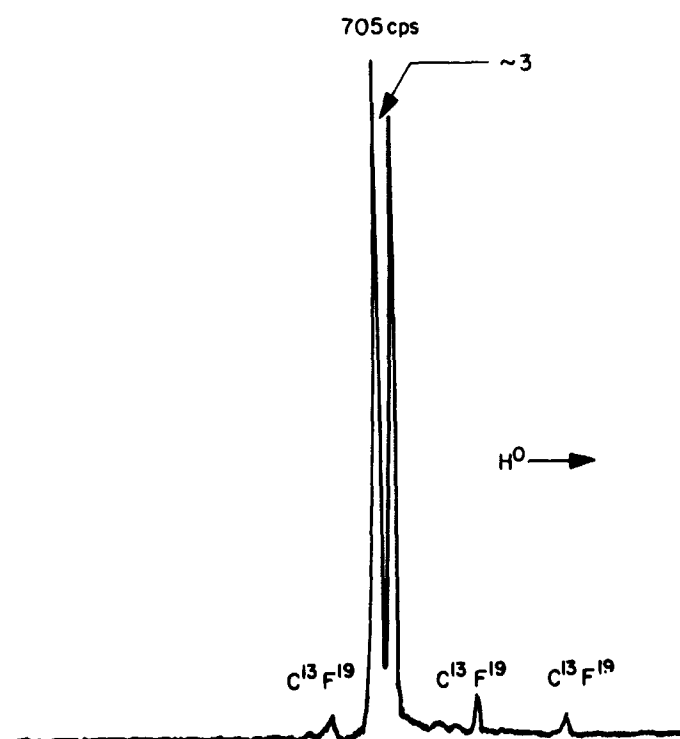


Fig. 9. F^{19} spectra of the adduct of 3-methyl-2-pentene and trifluorothioacetic acid (II)

A summary of the chemical shifts of (I), (II), and related derivatives is shown in Fig. 7. The total range of the chemical shifts observed is about 2500 cps at 56.4 Mc and a field of 14 kgauss.

D. Electronic Properties of TCNQ Complexes,

F. E. Stewart, A. Rembaum, and L. E. Creasy

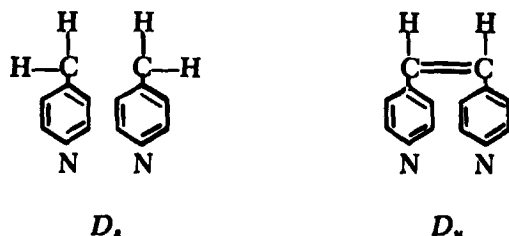
1. Introduction

The discovery of a pseudometallic behavior of heterocyclic organic salts (Refs. 27, 28, and 29) of general formula $D^+ (\text{TCNQ})^-$ TCNQ, in which D is an aromatic molecule generally containing a nitrogen atom, and TCNQ symbolizes the tetracyanoquinodimethane molecule, constitutes the most interesting development of the last decade in the area of electronic conductivity in organic systems.

This class of compounds exhibits room temperature conductivity ranging from 100 to about $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$, i.e., the highest conductivity of organic crystals synthesized to date. It was also shown recently (Ref. 28) that polymeric analogs of the TCNQ salts can be prepared. One such complex, copoly(styrene), 1-butyl-2-vinylpyridinium (TCNQ^-) TCNQ had a conductivity of $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and these polymeric complexes could be cast from solution as homogeneous films. The mechanism of electronic transport in the above monomeric or polymeric salts is not well understood.

In this report a study of the electrical properties of TCNQ complexes representing unit segments of nonconjugated as well as conjugated polymers is described.

The following two model compounds were chosen: a saturated donor 1, 2-bis-(4 pyridyl)-ethane, D_s ; and unsaturated donor 1, 2-bis-(4 pyridyl)-ethene, D_u .



Both structures D_s and D_u in form of their TCNQ salts exhibited high electrical conductivities only in the presence of neutral TCNQ, but no significant differences due to conjugation could be detected so far.

2. Experimental

Monomethyl iodonium salts were prepared by adding excess methyl iodide (8.52 g) to D_s or D_u (0.84 g) dissolved in benzene (50 ml). The TCNQ complexes were formed in a nitrogen atmosphere by adding Li TCNQ (0.42 g) in boiling ethanol (100 ml) to a hot solution of monomethyl iodonium salt (0.47 g) in ethanol (10 ml), according to a recently described procedure (Ref. 29). The elemental analyses of iodonium salts and TCNQ complexes were carried out by means of a F & M Model 185 CHN analyzer.

All visible spectra were determined with a Cary Model 14 spectrophotometer in spectral grade acetonitrile as solvent.

Conductivity measurements were made on 0.5-in.-D cylindrical pellets. Pellets prepared under pressures between 20,000 and 100,000 lb/in.² had essentially identical

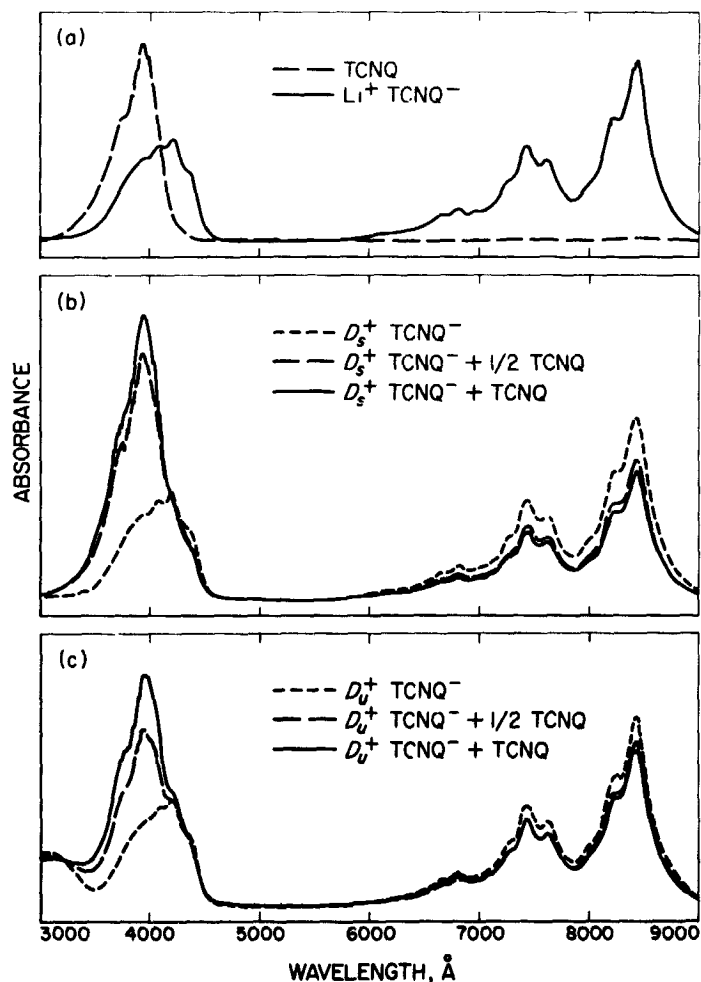


Fig. 10. Visible absorption spectra (10^{-5} M) in acetonitrile

conductivities. Electrical contact was made with vacuum-deposited gold electrodes. Using this technique, resistivity values could be reproduced within a factor of two. Silver paste or platinum disk contacts yielded much less reliable results. ESR measurements were made by a previously reported procedure (Ref. 30), on samples consisting of either small chips of compacted pellets, powdered complexes, or complexes dispersed in KCl. Pressure and grinding seemed to have no significant effect on the free spin concentration as derived from the ESR intensity.

3. Results and Discussion

a. Spectrophotometric data. Confirmation of the proposed structures of the synthesized complexes is provided by their visible absorption spectra. As shown in Fig. 10, the TCNQ radical anion absorbs strongly at 4200 Å ($\epsilon = 24,300$) and at 8420 Å ($\epsilon = 43,300$), while neutral TCNQ absorbs only at 3950 Å ($\epsilon = 63,600$). The intensity ratio of the 4200 and 8420 Å bands is approximately 0.57 for simple salts, and that of the 3950 and 8420 Å bands is approximately 2.0 for salts containing one neutral molecule of TCNQ per complex.

The spectrophotometric analysis agreed with the proposed radical anion-to-neutral acceptor ratio to within

about 5%. However, the elemental analysis (Table 5) agreed, on the average, with the theoretical percentages of C, H, and N to better than 1%.

b. Electrical properties. In Table 5 are listed the analytical results as well as room temperature resistivities and their activation energies E obtained by applying the formula $\rho = \rho_0 \exp(E/kT)$ from 77 to 300°K. Average values are quoted with deviations being less than 30% for ρ and 10% for E . Such deviations are presumably due to variations in intergranular resistances (Ref. 31). The addition of neutral TCNQ dramatically lowers the resistivity due to increased electron delocalization. The low activation energy of these latter complexes approaches that of metallic conduction behavior.

c. Electron spin resonance (ESR). Each of the four complexes studied here contains approximately Avagadro's number of unpaired electrons per mole at room temperature (Table 5). There is evidence that increased electron delocalization facilitates unpairing, since those complexes containing neutral TCNQ have considerably higher unpaired spin concentrations than those without neutral TCNQ. Relative spin concentrations quoted are considered accurate to 30%; however, absolute values are known only to within a factor of two.

Table 5. Electronic and magnetic properties of TCNQ-1 substituted pyridinium salts

Complexes	Calculated percentage				Experimental percentage				ρ at 25°C, ohm-cm	Resistivity activation energy E , ev	ESR intensity at 25°C, spins/mole $\times 10^{-23}$	Singlet- triplet separation energy J , ev	g value
	C	H	N	I	C	H	N	I					
D_2 Mono-iodonium salt	47.84	4.63	8.59	38.93	47.04 46.80	4.24 4.45	8.61 8.45	40.7					
D_2 Mono-iodonium salt	48.14	4.04	8.65	39.50	47.54 47.44	4.69 4.60	9.13 9.02	37.95					
$D_2^+TCNQ^-$	74.42	4.75	20.83	—	73.55 73.55	5.37 4.88	20.71 20.43	—	6.4×10^4	0.105	0.35	~ 0.03	2.0028
$D_2^+TCNQ^-$	74.80	4.27	20.94	—	72.68 72.90	4.64 4.39	21.19 21.09	—	6.4×10^4	0.145	1.5	~ 0.045	2.0028
$D_2^+TCNQ^-$ +TCNQ	73.15	3.79	23.06	—	72.12 72.28	3.66 3.74	24.89 24.84	—	3.4	0.035	11.7	0	$g_{11} = 2.0033$ $g_{\perp} = 2.0024$
$D_2^+TCNQ^-$ +TCNQ	73.39	3.48	23.14	—	74.32 74.20	3.61 3.65	23.96 23.67	—	3.8	0.035	8.0	0	$g_{11} = 2.0036$ $g_{\perp} = 2.0028$

Simple TCNQ salts follow a singlet-triplet model for paramagnetism in which the ESR intensity I is proportional to $T^{-1} [\exp (J/kT) + 3]^{-1}$. The singlet-triplet separation energy J may be calculated from the formula $J = 1.61 kT_m$, where T_m is the temperature at which I is

a maximum. We find for the D_s TCNQ and D_u TCNQ simple salts that T_m is considerably above ambient temperature and in the range in which these salts begin to decompose. Therefore an alternate procedure for determining J was attempted.

In the temperature range for which $J \gg kT$, the product $I \times T$ is proportional to $\exp (-J/kT)$, and a semilog plot of $I \times T$ versus T^{-1} will be a straight line the slope of which is $(J/k) \log e$. From such a plot (Fig. 11) the measured value of J was found to be not sufficiently large in comparison with kT to make the above approximation valid. We estimate that the measured value of J is too small by a factor of approximately two. It can only be concluded that J is probably somewhat smaller than 0.1 ev.

In the low-temperature region of Fig. 11 the triplet contribution to paramagnetism is small and the doublet impurity contribution predominates. In this region $I \times T$ is independent of temperature.

Complex TCNQ salts containing neutral TCNQ exhibit Pauli spin paramagnetism which is characteristic of a degenerate electron gas and operative in metals (Ref. 31). In this case the measured ESR intensity is independent of temperature. Such a paramagnetism was found for our complex salts (Table 5).

The shape of the ESR signal of the complex salts exhibits an interesting rotational anisotropy that has not

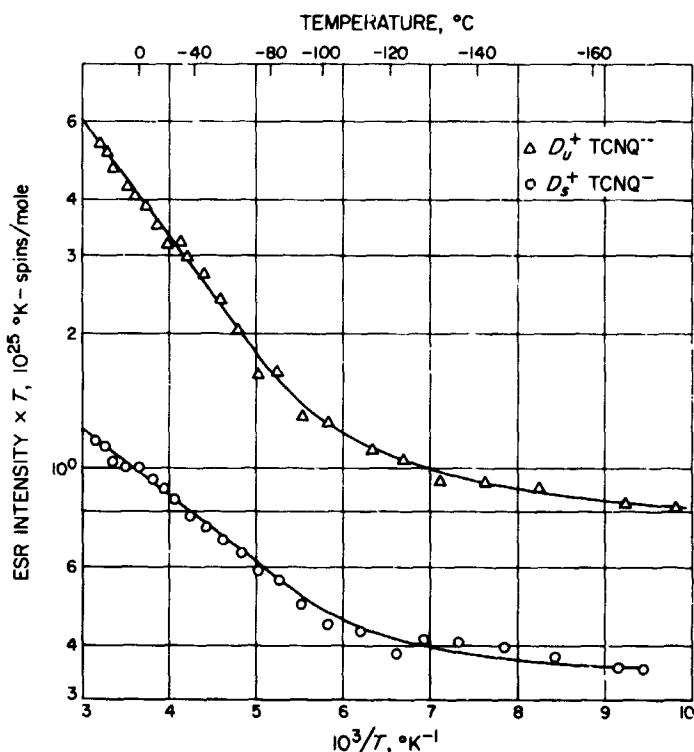


Fig. 11. Temperature dependence of ESR intensity for simple TCNQ salts

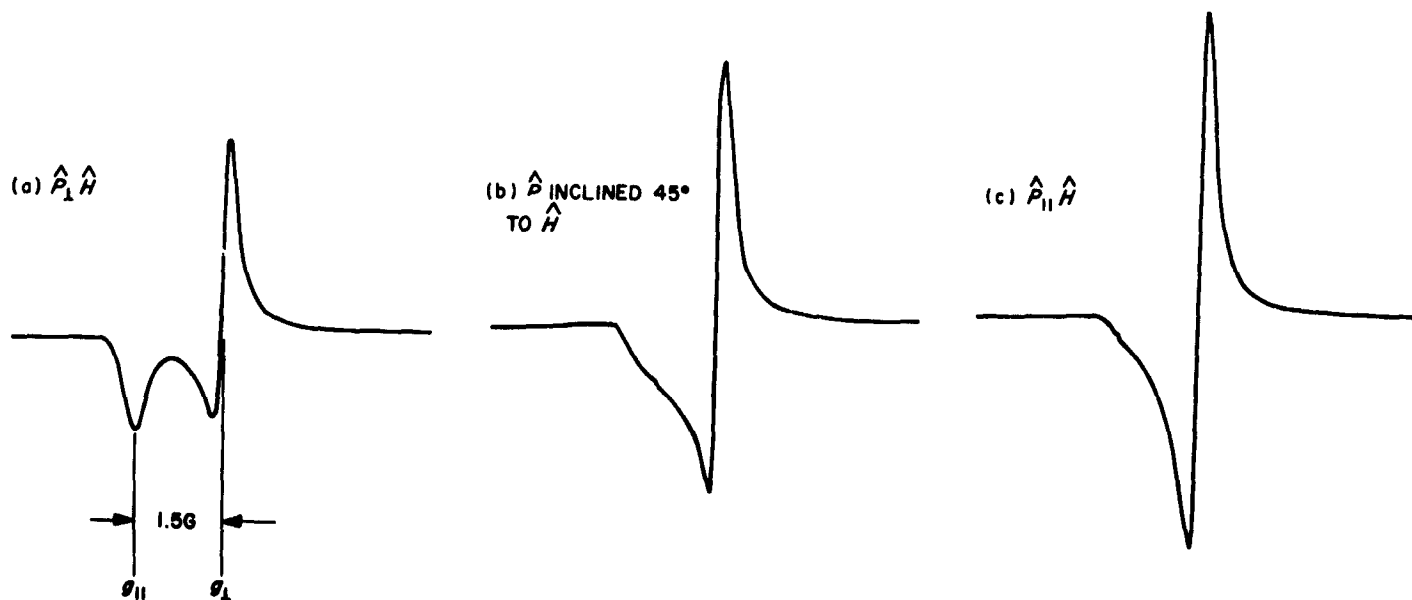


Fig. 12. Rotational anisotropy of a pellet of D_s TCNQ-TCNQ

been reported previously. If a pellet is oriented in the magnetic field in such a way that the direction in which the pressure was applied to it, $\hat{P}$, is kept perpendicular to the magnetic field $\hat{H}$, no line-shape change results; however, a change is observed when the pellet is rotated to make $\hat{P}$ parallel to $\hat{H}$ (Fig. 12). Such a change does not occur in the simple salts. Neither does it occur in the complex salts if they are in a powdered rather than in a compacted form. The ESR signal shape for $\hat{P} \parallel \hat{H}$ (Fig. 3a) is similar to that of a single crystal having axial symmetry and an anisotropic g value. Single crystals of organic TCNQ salts are known to have anisotropic g values but compacted pellets, usually composed of many microcrystals randomly oriented, are not known to exhibit rotational anisotropy. It would appear that under pressure the molecules of our complex salts assume a preferred orientation resulting in an axial symmetry. Investigations are in progress to establish a correlation between the anisotropy of a compressed pellet and its electronic conductivity.

E. Reactions of Carboxyl-Terminated Prepolymers With Polyaziridines and Polyepoxides,

S. H. Kalfayan and B. A. Campbell

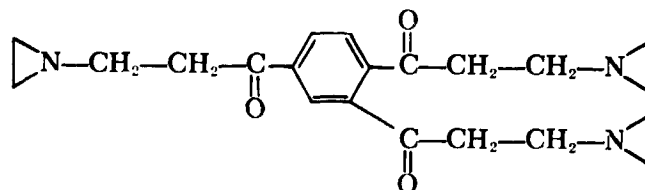
1. Introduction

The study of the reactions of carboxyl-ending polyether and hydrocarbon backbone prepolymers with aziridines and epoxides was continued. A novel trifunctional aziridine, 1,2,4-*tris* 2-(1-aziridinyl) ethyl trimellitate was evaluated as a crosslinking agent. Two carboxyl-ending poly(propylene oxides), products of the condensation of succinic and adipic acids with PPO 1000, discussed in Section XI-F in this SPS issue, were reacted with different aziridines and epoxides. A condensation product of diethylene glycol and the dimer fatty acid, Empol 1010, was also evaluated. These investigations are of a preliminary nature and are part of the overall objectives of studying the effect of backbone structure on the properties of an elastomer and investigating the products obtained for possible use as propellant binders.

2. Experimental

a. Materials. Many of the materials used were described previously (SPS 37-39, 37-40, 37-41, Vol. IV). The new ones are as follows:

- (1) 1,2,4-*tris* 2-(1-aziridinyl) ethyl trimellitate (Dow Chemical Co., NC 1455), structural formula:



- (2) Carboxyl-ending PPO 1000-succinic acid condensate (PPO-COOH-S), equiv. wt. 1200.
- (3) Carboxyl-ending PPO 1000-adipic acid condensate (PPO-COOH-A), equiv. wt. 870.
- (4) Carboxyl-ending diethylene glycol-Empol 1010 condensate, equiv. wt. 590.

NC 1455 was used as received. Stoichiometric amounts were employed in all cases.

b. Preparation and characterization of the condensates.

All three carboxyl-ending prepolymers were prepared by Fischer esterification in dry xylene. The milder *p*-toluenesulfonic acid was used as catalyst, instead of a mineral acid. Water from the condensation reaction was removed by fractional distillation as the reaction proceeded. The products were analyzed for acidity, hydroxyl content (acetylation method) and molecular weight (vapor pressure osmometry).

3. Results and Discussion

a. Reactions of PPO-COOH-S and PPO-COOH-A with aziridines and epoxides. Results for these reactions are given in Tables 6 and 7. Cures could be obtained with

Table 6. Curing of succinic and adipic acid condensates of PPO 1000 with polyaziridines

Prepolymer	Curing agent	Gel time at 100°C	Shore A hardness	
			24 hr at 100°C	48 hr at 100°C
PPO-COOH-S ^a	HX 740	>48 hr	thick fluid	thick fluid
	ZC 466	3¾ hr	10	10
	MAPO	1 hr	reverts to fluid	
	NC 1455	5 min	37	37
PPO-COOH-A ^b	HX 740	1½ hr	reverts to fluid	
	ZC 466	1¾ hr	17	17
	MAPO	1 hr	reverts to fluid	
	NC 1455	8 min	45	47
	NC 1455	20 min	25	37
	ZC 466			

^a Succinic acid condensate.
^b Adipic acid condensate.

Table 7. Curing of succinic and adipic acid condensates of PPO 1000 with polyepoxides

Prepolymer	Curing agent	Gel time at 150°C, hr	Shore A hardness		
			24 hr at 100°C	48 hr at 100°C	48 hr at 150°C
PPO-COOH-S ^a	ERL 0510 Shell X 801	>2 <17 >48	fluid fluid	fluid fluid	soft soft
PPO-COOH-A ^b	ERL 0510 Shell X 801	>4 <23 >48	fluid fluid	soft fluid	2 thick fluid

^aSuccinic acid condensate.
^bAdipic acid condensate.

Table 8. Curing of Empol 1010 condensate of diethylene glycol with polyaziridines and polyepoxides

Curing agent	Gel time,		Shore A hardness			
	at 100°C	at 150°C	24 hr at 100°C	48 hr at 100°C	24 hr at 150°C	48 hr at 150°C
HX 740	3¼ hr		soft	soft		
ZC 466	¾ hr		20	24		
MAPO	1 hr		soft	soft		
NC 1455	5 min		50	55		
NC 1455 } ZC 466 }	7 min		31	40		
ERC 0510	5½ hr	2½ hr	10	13	27	37
Shell X 801	>48 hr	>8 <22 hr	fluid	fluid	1	23
Epon 828	>48 hr	>32 <48 hr	fluid	fluid	—	soft

the triaziridine NC 1455 and the diaziridine ZC 466. The triaziridine MAPO gelled the prepolymers, but further heating at 100°C caused liquefaction. The diaziridine HX 740 did not gel the PPO-COOH-S and gelled the PPO-COOH-A, but the gel liquefied on prolonged heating at 100°C. These results seem perplexing.

The functionalities of PPO-COOH-S and PPO-COOH-A, calculated from molecular weights determined by vapor pressure osmometry (VPO), were 1.4 and 1.7, respectively. A triaziridine would be capable of curing prepolymers of low functionality, but a diaziridine would not be capable. The fact that NC 1455 gave cures and HX 740 did not, is explainable on the functionality basis; but the observation that MAPO-cured products reverted and ZC-466-cured ones did not, should have a different explanation. One possible explanation could be that both HX 740 and MAPO, because of their imide-type linkages, form oxazolines on heating in the presence of the acidic prepolymers. Oxazoline formation reduces the aziridine functionality and prevents cure. NC 1455 and ZC 466 are not capable of oxazoline ring formation.

It should also be mentioned that the accuracy of molecular weight determinations by the VPO method is greatly affected by the presence of low molecular weight impurities. The functionality values given above should not be considered as altogether accurate.

Satisfactory cures could not be obtained with both the triepoxides used.

b. Reactions of Empol 1010-diethylene glycol condensate with aziridines and epoxides. The results of these experiments are summarized in Table 8. The functionality of the prepolymer, calculated from the VPO molecular weight was 2.2. Gelation occurred with all the aziridines, but cures with MAPO and HX 740 resulted in soft products, showing the same tendency observed with the PPO condensates. The product obtained from ZC 466 was highly extensible. NC 1455 gave a harder product with low elongation. Products obtained from a mixture of ZC 466 and NC 1455 in 1:1 equivalent ratios, had intermediate properties.

Satisfactory cures were obtainable after 48 hr at 150°C from the triepoxides ERL 0510 and Shell X 801, but the products had low tear and elongation.

c. Reaction of NC 1455 with carboxyl-ending polybutadienes. Immediate gelation occurred when NC 1455 and carboxyl-ending polybutadiene mixtures were exposed to 100°C. The mixtures thickened at room temperature and pot lives were short (30 to 40 min). Gelation at room temperature occurred within 2 to 5 hr (Table 9). NC 1455 can be useful for curing compositions at low temperatures.

Table 9. Curing of carboxyl-ending polybutadienes with NC 1455

Prepolymer	Gel time at 100°C	Gel time, at room temperature, hr	Shore A hardness	
			24 hr at 100°C	48 hr at 100°C
Telagen CT	Immediate	2½	30	31
Butarez CTL	Immediate	2	46	46
HC 434	Immediate	5	55	55

F. Carboxyl-Ending Poly(Alkylene Oxides),

S. H. Kalfayan

1. Introduction

The comparative study of the effects of backbone structure on the properties of an elastomer is of interest. The polyether and hydrocarbon backbones are the ones presently under study. To obviate the consideration of the influence of the type of crosslink, it is necessary that both types of polymer possess the same kind of functional group and be extended or crosslinked by the same reagents.

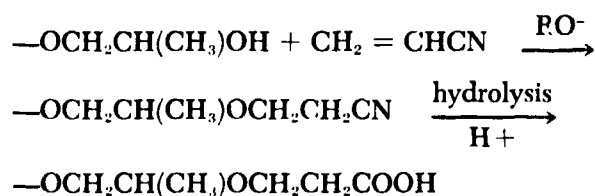
Carboxyl-ending, unsaturated hydrocarbon backbone prepolymers have been commercially available for some time and are suitable for the kind of study desired. These are butadiene-based polymers, of number average molecular weights M_n ranging from 1000 to 6000. Carboxyl-ending polyether backbone prepolymers have to be prepared. Several seemingly feasible methods, all using poly(alkylene oxides) (PAO) as starting materials, were tried. Of these methods the cyanoethylation of PAO followed by hydrolysis of the cyano-ending intermediate was reported previously in several SPS's. Two others, the haloform and the esterification methods, are discussed presently. The haloform method is applicable only to

PAO with secondary hydroxyl groups, with the secondary carbon atom attached to one methyl group. Poly(propylene oxide), PPO, of M_n 1000 fulfills this requirement. The esterification method, using dibasic acids, is applicable to both poly(ethylene oxides) (primary hydroxyls) and to PPO (secondary hydroxyls). A brief review of the cyanoethylation-hydrolysis method is also included in the discussion that follows:

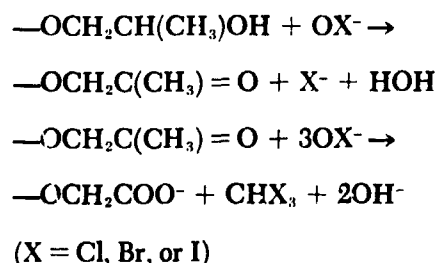
2. Discussion

The equations that represent the three methods employed to modify the OH end-groups of PPO 1000 to carboxyl groups are as follows:

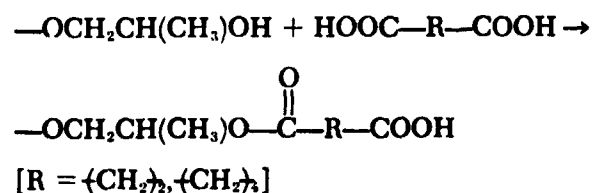
(1) Cyanoethylation and hydrolysis



(2) Haloform reaction



(3) Esterification



a. Cyanoethylation and hydrolysis. Extensive study of this method showed that cyanoethylation could be carried out up to 95% completion, and that complicating side reactions such as block polymer formation with acrylonitrile could be minimized. During hydrolysis, however, cleavage of the alkoxy group introduced by cyanoethylation took place, resulting in partial reversion to the original PPO. The purification of the dicarboxylic acid was tedious and incomplete. End-group analysis showed the presence of about 15–18% of hydroxyl-terminated material considered to be monocarboxylated PPO.

b. The haloform reaction. This reaction was carried out with disecundary dipropylene glycol (DPO) as well as with PPO 1000, using sodium hypoiodite, formed *in situ* from iodine and NaOH. The haloform (iodoform) reaction, a commonly used test in organic analysis for the identification of $\text{CH}_3-\text{C}=\text{O}$ group or compounds which can yield this group on reaction with the reagent, involves also the formation of the salt of an acid, as well as the iodoform. The conversion of DPO to the corresponding acid, based on the weight of iodoform obtained, averaged to 20%. That of PPO averaged to about 10%. When reaction mixtures were warmed to increase the rate and the yield, more iodine was consumed than accounted for by the amount of iodoform obtained, indicating the probability of iodination of the chain, or the formation of iodate, or both. The haloform reaction, applied as a preparative method for the carboxylic acids desired, shows little value.

c. Esterification. PPO 1000 was esterified with both succinic and adipic acids in dry xylene, using excess of the dibasic acids (2.5 equivalents of COOH to 1.0 equivalent of OH), in presence of toluenesulfonic acid as catalyst. The water formed was removed by fractional distillation as the condensation reaction proceeded. Seventy percent of the water could be removed during the first hour of refluxing. The results obtained for some of the runs are given in Table 10.

It must be noted that molecular weight M_n determinations by vapor pressure osmometry (VPO) can lead to large errors if low molecular weight impurities are present in the analyzed prepolymer. The presence of unreacted acid in the preparations of Table 10 is a possibility, although repeated extractions with water, to remove the suspected impurities and prolonged drying in vacuum were carried out with each run. The molecular weight values as well as the functionality values which were based on the former, should not be regarded as un-

suspect. The hydroxyl contents reported are the lowest concentrations detectable by the method used. The acetylation method was used for the first four runs. A colorimetric method was employed for the last run. These results indicate that probably all the OH terminals of PPO 1000 were reacted.

3. Conclusion

Of the three methods used to prepare carboxyl-terminated PPO, condensation with dibasic acids is the simplest and the most promising.

G. Method for Estimating the Temperature-Dependence of Foam Diffusion Constants, E. F. Cuddihy and J. Moacanin

It has been shown (Ref. 33, and SPS 37-34 through 39, Vol. IV) that the diffusion of gases in rigid, cellular foams obey Fick's Law and that the diffusion coefficient D_f can be predicted from the following expression

$$D_f = \left(\frac{3RT}{M} \right) (\rho_0/\rho) P_e \quad (1)$$

where

D_f = diffusion coefficient of the foam

P_e = permeation constant of the solid polymer gas system

ρ_0 = density of the solid polymer

ρ = density of the foam

T = absolute temperature

M = mol wt of the diffusing gas

R = gas constant

Table 10. Esterification of PPO 1000 with dibasic acids ($\text{OH}/\text{COOH} = 1/2.5$)

Run No.	Acid	Reflux time at 135-138°C, hr	Acidity, meq/g	OH content, meq/g	Molecular weight by VPO	Equivalent weight	Functionality, $\frac{\text{mol wt}}{\text{equiv wt}}$
1	Succinic	5	0.83	<0.1	—	1205	—
2	Succinic	8.5	0.86	<0.1	1660	1162	1.42
3	Adipic	4	1.07	<0.1	—	34	—
4	Adipic	10	1.15	<0.1	1482	870	1.70
5	Adipic	14	1.01	<0.05	1706	990	1.72

The validity of this equation was confirmed at room temperature from experimentally measured values of D_f as a function of ρ .

Using Eq. (1), it should also be possible to evaluate D_f at any temperature from the knowledge of the temperature dependence of P_e , which is known (Ref. 34) to obey an Arrhenius relation

$$P_e = P_{e0} \exp(-\Delta H_p/RT) \quad (2)$$

where ΔH_p is the activation energy of permeation. Substituting Eq. (2) into Eq. (1) and rearranging results in

$$\ln \frac{D_f}{T} = -\frac{\Delta H_p}{RT} + \ln \left(\frac{3R\rho_0 P_{e0}}{M\rho} \right) \quad (3)$$

Inasmuch as the ratio ρ_0/ρ is temperature independent, the last term is a constant and hence a straight line relationship between $\ln D_f/T$ and $1/T$ is predicted.

Table 11. Diffusion constants of a polyurethane foam^a at various temperatures

Temperature, °C	$D \times 10^4$ cm ² /sec	$D/T \times 10^9$ cm ² /sec °K	$1/T \times 10^3$
22	1.76	5.96	3.39
41	3.34	10.6	3.18
61	9.57	28.6	2.99
81	13.7	38.7	2.82

^aEmerson and Cummings, Inc., Eccofoam FPH/12/6H, density=4.5 lb/ft³

In Table 11 are given values of D_f obtained at four temperatures for a rigid, closed-cell (>95%) polyurethane foam of density 4.5 lb/ft³ (Emerson and Cummings, Incorp., Eccofoam FPH/12/6H). The experimental details are reported in SPS 37-35, Vol. IV. The data which are plotted in Fig. 13 as $\ln D_f/T$ versus $1/T$ show a reasonably good straight line relationship. The slope yields for ΔH_p a value of 7.4 kcal/mole. This value is in excellent agreement with the usual 6 to 12 kcal/mole range for the activation energies for diffusion processes in polymers (Ref. 34).

For the particular case of the permeation of CO₂ through a rigid polyurethane, no data were found in the

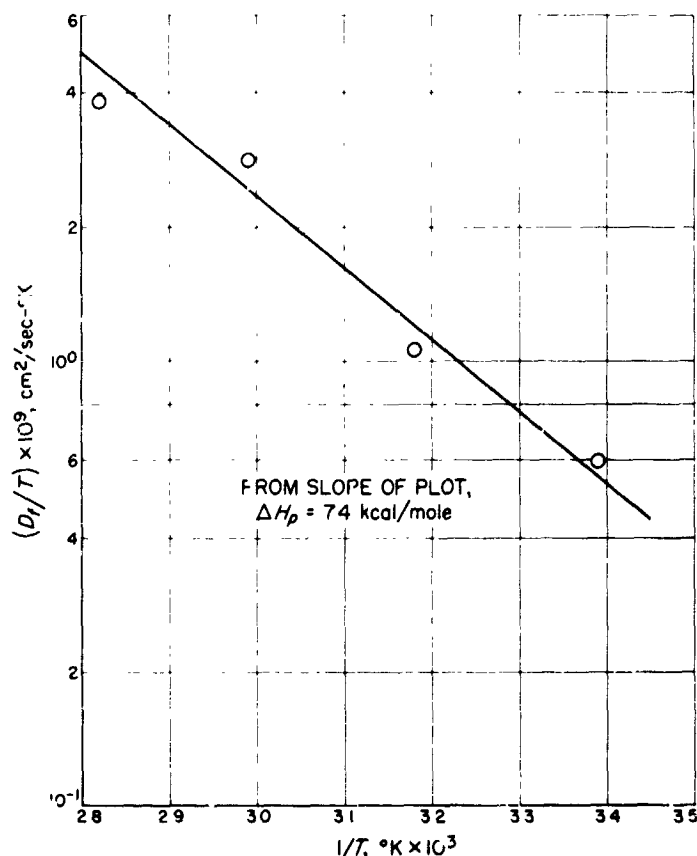


Fig. 13. Temperature dependence of the diffusion coefficient for a CO₂-filled rigid polyurethane foam, density 4.5 lb/ft³

literature. However, some data (Ref. 35) were found for a rubbery polyurethane, and these are given in Table 12. The activation energy for permeation ΔH_p was found to be 9.4 kcal/mole, and this compares favorably with the

Table 12. Results for CO₂ permeation through a rubbery polyurethane^a

Temperature, °C	$P_e \times 10^5$ (cm ³ STP) mm cm ² -sec-cmHg	$D \times 10^4$ cm ² /sec	Solubility, l.m ³ STP/cm ³ -atm
25	1.65	0.094	1.50
50	6.34	0.440	1.10
Activation energies, kcal/mole			
$\Delta H_p = 9.4$ (for permeation)			
$\Delta H_d = 11.7$ (for diffusion)			
$\Delta H_s = -2.3$ (for solubility)			

^aData for Volcprene polyurethane rubber (Ref. 35)

value of 7.4 kcal/mole. Further, it is expected that ΔH_p for the rigid polyurethane should be lower than that for the rubbery polyurethane, since it has been adequately verified (Ref. 34) that the activation energy of a polymer above its T_g is higher than that value obtained when the polymer is below its T_g . Hence the 9.4 kcal/mole corresponds to a polyurethane above T_g , whereas the 7.4 kcal/mole is for a polyurethane below T_g .

In conclusion, we have shown that the equation

$$D_f = \left(\frac{3RT}{M} \right) (\rho_0/\rho) P_{e0} \exp(-\Delta H_p/RT)$$

adequately describes the temperature dependence of the foam diffusion constant.

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